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An empirical method for the prediction of overall relaxation time τ_{mix} of polar liquid mixtures at microwave frequencies

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Abstract : Experimental data on thirteen binary mixtures of polar liquids containing associative and non-associative molecules have been examined for their dielectric behaviour at microwave frequencies. The values for the overall relaxation times of the various binary mixtures are calculated by the simple mixing rule, reciprocal mixing rule and an empirical relation suggested in this paper. The τ_{mix} values so computed indicate that while S.M. rule and R.M. rule are not dependable, the empirical relation suggested here is quite satisfactory in predicting the τ_{mix} values.

Keywords : Binary mixtures, polar liquids, associative. non-associative, dielectric behaviour, relaxation times.

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1. Introduction

The dielectric behaviour of two component polar liquid systems has been the subject of current interest. The knowledge of the overall relaxation time τ_{mix} for a binary mixture composed of two different polar molecules in dilute solutions of non-polar solvents, as a function of composition may be useful for better understanding of the relaxation behaviour of one set of polar molecules in presence of other set of polar molecules having different size, shape and dipole moment. At present the experimental data available for the relaxation behaviour of mixtures is very limited. The methods of prediction and calculations may prove to be very useful.

The endeavour of the present article is to pull together all the available data on binary mixtures to ascertain the validity of various methods for predicting τ_{mix} values ; to bring into light the discrepancies present in the existing data and finally to formulate an empirical relation which can predict the experimental results more precisely.

2. Empirical relation

Recently, we have (Sharma and Gandhi 1987) employed three methods of predicting τ_{mix} viz. simple mixing rule, reciprocal mixing rule and a procedure suggested by Madan (1983, 1980) for various binary systems and have found that although simple mixing rule is slightly better, yet none of these procedures can successfully predict the experimental data. These results of course suggest that an expression similar to the simple mixing rule may be more successful in predicting the experimental values, provided it involves a term which can take care of the various factors such as shape, size, viscosity and associating dipole moments which affect the molecular environment.

Let there be a single component system of overall relaxation time τ_1 and let another component of relaxation time τ_2 be added to it. The presence of the 2nd component will change the molecular environment and as a result τ_1 will change to τ_{mix} so that τ_{mix} can be written as

$$\tau_{mix} = \tau_1 + \tau' \tag{1}$$

where $\tau' = (\tau_{mix} - \tau_1)$ and represents a time which will depend on the mole fraction x_2 of the second component, the overall relaxation time τ_2 of the second component and the characteristic properties of the binary system. τ' then can be written as

$$\tau' = Ax_2\tau_2 \tag{2}$$

Here A is constant characteristic of the binary system. Combining eqs. (1) and (2), τ_{mix} becomes

$$\tau_{mix} = \tau_1 + Ax_2\tau_2 \tag{3}$$

Eq. (3) is nothing but a form of the simple mixing rule in which a term A has been introduced assuming that this term can take care of the various factors which influence the molecular environment. The characteristic constant A can assume both positive as well as negative values depending on the characteristic nature of the binary system and can be determined from one known experimental τ_{mix} value using eq. (3). The value of A, so obtained can then be used to predict τ_{mix} values at other compositions employing eq. (3).

3. Results and discussion

The theoretically calculated τ_{mix} values employing simple mixing rule, reciprocal mixing rule and empirical relation of eq. (3) for the various experimental data available in literature are listed in Tables 1 to 13. The values of the characteristic constant A of the binary systems employing experimental τ_{mix} value at a composition of nearly 50-50 moles of the two components for each system are reported

in Table 14. The first four tables report data on non-associative+non-associative systems, Tables 5 to 10 list the data on associative+associative systems and Tables 11 to 13 record data on associative+non-associative systems.

Table 1. Experimental* and theoretically calculated values of τ_{mix} by different methods for (benzophenone–tetrahydrofuran) system at 20°C.

Temp. (°C)	Mole fraction of benzophenone in (benzophenone+tetrahydrofuran)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S.M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R.M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E.R.) in secs	% of dev. of τ_{cal_1} (S.M.)	% of dev. of τ_{cal_2} (R.M.)	% of dev. of τ_{cal_3} (E.R.)
	0.00	3.0	—	—	—	—	—	—
	0.108	2.96	4.96	3.30	3.03	67.57	11.49	2.37
20	0.235	2.97	7.27	3.76	3.06	145.78	26.60	3.03
	0.492	3.13	11.95	5.19	3,13	281.79	65.82	0
	1.00	21.2	—	—	—	—	—	—

*Data by Kilp *at el* (1966).

Table 2. Experimental* and theoretically calculated values of τ_{mix} by different methods for (chloroform–chlorobenzene) system at 30°C.

Temp. (°C)	Mole fraction of chloroform in (chloroform+chlorobenzene)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E. R.)
	0.0000	10.3	—	—	—	—	—	—
	0.5259	9.0	7.7	7.0	9.0	14.4	22.2	0
30	0.7008	9.9	6.9	6.3	8.6	30.3	36.4	13.1
	0.7973	10.7	6.4	6.0	8.3	40.2	43.9	22.4
	1.0000	5.4	—	—	—	—	—	—

*Data by Srivastava and Sinha (1982).

Table 3. Experimental* and theoretically calculated values of τ_{mix} by different methods for (bromoform–chlorobenzene) system at 30 C.

Temp. (°C)	Mole fraction of bromoform in (bromoform+chlorobenzene)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E. R.)
	0.0000	10.3	—	—	—	—	—	—
	0.4532	12.1	16.7	14.0	12.95	38.2	15.7	7.02
30	0.5648	13.6	18.3	15.3	13.6	34.6	12.5	0.0
	0.6872	15.7	20.0	17.1	14.32	27.4	8.9	−8.79
	1.0000	24.4	—	—	—	—	—	—

*Data by Srivastava and Sinha (1982).

Table 4. Experimental* and theoretically calculated values of τ_{mix} by different methods for (bromobenzene – chlorobenzene) system at 30°C.

Temp. (°C)	Mole fraction of bromobenzene in (bromobenzene + chlorobenzene)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) In secs	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E. M.)
30	0.0000	10.3	—	—	—	—	—	—
	0.1519	11.5	11.2	10.9	11.57	2.6	5.2	0.61
	0.3463	13.2	12.4	11.8	13.2	6.1	10.6	0.0
	0.6138	16.0	14.0	13.4	15.44	12.5	16.3	3.5
	1.0000	16.4	—	—	—	—	—	—

*Data by Srivastava et *al* (1985).

Table 5. Experimental* and theoretically calculated values of τ_{mix} by different methods for (*n*-propanol – butanediol-1,3) system at different temperatures.

Temp. (°C)	Mole fraction of butanediol-1,3 in (*n*-propanol + butanediol-1,3)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E. R.)
-75.0	0.00	3.07	—	—	—	—	—	—
-71.2	0.10	3.20	5.89	5.63	3.14	84.1	75.9	1.88
-60.0	0.25	3.12	5.42	4.94	3.25	73.7	58.3	4.17
-53.4	0.35	3.75	5.11	4.57	3.32	36.3	21.9	11.5
47.5	0.45	3.37	4.79	4.25	3.39	42.1	26.1	0.59
-42.8	0.55	3.46	4.48	3.97	3.46	29.5	14.7	0
-34.8	0.75	4.22	3.85	3.51	3.60	8.8	16.8	-14.69
-30.4	0.90	6.05	3.38	3.23	3.71	44.1	46.6	-38.67
-27.5	1.00	6.20	—	—	—	—	—	—

*Data by McDuffie et *al* (1963).

Table 6. Experimental* and theoretically calculated values of τ_{mix} by different methods for (glycerol – *n*-propanol) system at different temperatures.

Temp. (°C)	Mole fraction of glycerol in (glycerol + *n*-propanol)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E. R.)
-75.0	0.00	3.07	—	—	—	—	—	—
-70.0	0.05	2.04	4.02	4.01	2.97	97.1	96.6	45.59
-55.0	0.15	1.97	3.92	3.88	2.77	98.9	97.0	40.61
-49.9	0.20	1.75	3.87	3.82	2.68	121.1	118.3	53.1
-42.0	0.30	2.11	3.77	3.71	2.48	78.7	75.8	17.54
-23.4	0.60	1.90	3.47	3.41	1.90	82.6	79.5	0.0
-15.6	0.80	1.91	3.27	3.23	1.51	71.2	69.1	-20.9
-11.0	1.00	4.07	—	—	—	—	—	—

*Data by McDuffie et *al* (1963).

Table 7. Experimental* and theoretically calculated values of τ_{mix} by different methods for (1,2-propanediol + dipropylene glycol) system at 30°C.

Temp. (°C)	Mole fraction of dipropylene glycol in (1,2-propanediol + dipropylene glycol)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E R.)
	0.000	240	—	—	—	—	—	—
	0.157	302	395.4	274.7	338.06	30.9	9.0	11.94
30	0.359	417	595.4	337.5	464.23	42.8	19.1	11.33
	0.626	631	859.7	483.7	631,0	36.2	23.3	0
	1.000	1230	—	—	—	—	—	—

*Data by Rajyam *at al* (1980).

Table 8. Experimental* and theoretically calculated values of τ_{mix} by different methods for (IMA + BA) system at different temperatures.

Temp. (°C)	Mole fraction of IMA in (IMA + BA)	$\tau_0 \times 10^{12}$. exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs)	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M)	% of dev. of τ_{cal_3} (E. R.)
30	0.00	6.4	—	—	—	—	—	—
	0.24	7.7	7.7	7.2	7.7	0	-6.49	0
	0.49	9.1	9.0	8.2	9.1	-1.1	-9.89	0
	0.73	10.4	10.3	9.6	10.4	-0.96	-7.69	0
	1.00	11.7	—	—	—	—	—	—
40	0.00	5.2	—	—	—	—	—	—
	0.24	6.2	6.2	5.8	6.3	0	-6.45	1.61
	0.49	7.4	7.3	6.7	7.4	-1.35	-9.46	0
	0.73	8.4	8.3	7.7	8.5	-1.19	-8.33	1.19
	1.00	9.4	—	—	—	—	—	—
50	0.00	4.5	—	—	—	—	—	—
	0.24	5.3	5.2	5.0	5.3	-1.89	-5.66	0
	0.49	6.1	6.0	5.6	6.1	-1 64	-8.20	0
	0.73	6.7	6.7	6.4	6.9	0	-4.48	2.98
	1.00	7.5	—	—	—	—	—	—
60	0.00	3.8	—	—	—	—	—	—
	0.24	4.5	4.5	4.2	4.5	0	-6.67	0
	0.49	5.2	5.1	4.8	5.2	-1.92	-7.69	0
	0.73	5.8	5.8	5.5	5.9	0	-5.17	1.72
	1.00	6.5	—	—	—	—	—	—

*Data by Sharma and Gandhi (1989).

Among the four non-associative+non-associative systems studied here, the experimental data for benzophenone+tetrahydrofuran at 20°C are reported by Kilp *et al* (1966), for chloroform+chlorobenzene and bromoform+chlorobenzene systems both at 30°C by Srivastava and Sinha (1982), for bromobenzene+chlorobenzene at 30°C by Srivastava *et al* (1985). An examination of the data listed in Tables 1 to 4 shows that for all the four systems the theoretically calculated

Table 9. Experimental* and theoretically calculated values of τ_{mix} by different methods for (IMA+IA) system at different temperatures.

Temp. (°C)	Mole fraction of IMA in (IMA+IA)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E R.)
30	0.00	6.9	—	—	—	—	—	—
	0.26	8.6	8.2	7.7	8 1	-4.65	-10.47	-1.22
	0.54	9.3	9.5	8.9	9.3	2.15	4.30	0.0
	0 79	11.0	10.7	10.2	10.4	-2.73	-7.27	-5.45
	1.00	11.7	—	—	—	—	—	—
40	0.00	5.6				—	—	—
	0.26	6.6	6.6	6.3	6.6	0.0	-4.55	0.0
	0.54	7.6	7.7	7.2	7.6	1.32	-5.26	0
	0.79	8.6	8.6	8.2	8.5	0	-4.65	-1.16
	1.00	9.4	—	—	—	—	—	—
50	0.00	4.3				—	—	—
	0.26	5.1	5.1	4.8	5.1	0.0	-5.88	0.0
	0.54	5.9	6.0	5.6	5.9	1.69	-5.08	0.0
	0.79	6.7	6.8	6.5	6.6	1.49	-2.99	-1.49
	1.00	7.5	—	—	—	—	—	—
60	0.00	3.7		—	—	—	—	—
	0.26	4.5	4.4	4.2	4.4	-2.22	-6.67	-2.22
	0.54	5.2	5.2	4.8	5.2	0.0	-7.69	0.0
	0.79	6.0	5.9	5.6	5.9	-1.67	-6.67	-1.67
	1.00	6.5	—	—	—	—	—	—

*Data by Sharma and Gandhi (1989).

values by the empirical relation of eq. (3) exhibit much better agreement with the experimental values than those calculated by S. M. and R. M. rules. The absolute average percentage deviations for the benzophenone+tetrahydrofuran system are respectively 165.1, 34.6 and 1.8 for the S. M., R. M. and eq. (3) methods. For the chloroform+chlorobenzene system these are respectively 28.3, 34.2 and 11.8 ; for the bromoform+chlorobenzene system the corresponding values are 33.4, 12.4 and 5.3 and for the bromobenzene+chlorobenzene system these percentage deviations are 7.1, 10.7 and 1.4 respectively.

The data on binary systems of associative+associative components are reported by McDuffie *et al* (1963) for the (*n*-propanol+butanediol-1,3) and (glycerol+*n*-propanol) systems at different temperatures ; for the (1,2-propanediol+dipropylene glycerol) by Rajyam *et al* (1980) at 30°C, for the (isobutyl-methacrylate+*n*-butyl-acrylate) for the (isobutyl-methacrylate+isobutyl-acrylate) and for the (*n*-butyl-acrylate+isobutyl-acrylate) systems by Sharma and Gandhi (1989) at 30, 40,

Table 10. *Experimental and theoretically calculated values of τ_{mix} by different methods for (BA+IA) system at different temperatures.

Temp. (°C)	Mole fraction of IA (BA+IA)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E. R.)
30	0.00	6.4	—	—	—	—	—	-
	0.13	6.5	6.5	6.5	6.5	0.0	0.0	0.0
	0.37	6.7	6.6	6.6	6.7	-1.49	-1.49	0.0
	0.68	6.8	6.7	6.7	7.0	-1.47	-1.47	2.94
	1.00	6.9	—	—	—	—	—	—
40	0.00	5.2	—	—		—	—	—
	0.13	5.3	5.3	5.2	5.3	0.0	-1.87	0.0
	0 37	5.5	5.4	5.3	5.5	-1.82	3.64	0.0
	0.68	5.6	5.5	5.5	5.8	-1.79	-1.79	3.6
	1.00	5.6	-	—	-	—	—	—
50	0.00	4.5	—	—	—	-	—	—
	0.13	4.5	4.5	4.5	4.5	0.0	0.0	0.0
	0.37	4.4	4.4	4.4	4.4	0.0	0.0	0.0
	0.68	4.4	4.4	4.4	4.3	0.0	0.0	2.27
	1.00	4.3	—	—	—	—	—	—
60	0.00	3.8	—	—	—	—	—	—
	0.13	3.8	3.8	3.8	3.8	0.0	0.0	0.0
	0.37	3.7	3.8	3.8	3.7	2.70	2.70	0.0
	0.68	3.7	3.7	3.7	3.6	0.0	0.0	2.70
	1.00	3.7	-	—	—	—	—	—

*Data by Sharma and Gandhi (1989).

50 and 60°C. Here again, it is obvious from the values recorded in Tables 5 to 10 that S.M. and R.M. methods are unsuccessful in predicting the experimental results. However, the τ_{mix} values calculated by using eq. (3) predict the experimental results within moderate deviations. In order of S.M., R.M and eq. (3) methods, the average percentage deviations of the calculated values from the experimental ones are 45.5, 37.2 and 10.2 for the (*n*-propanol+butanediol-1,3) system 91.6, 89.4 and 29.6 for the (glycerol+*n*-propanol) system ; 36.6,

17.1 and 7.8 for the (1,2-propanediol + dipropylene glycerol) system ; 0.7, 8.0 and 0.0 at 30°C ; 0.9, 8.1 and 0.9 at 40°C ; 1.2, 6.1 and 1.0 at 50°C and 0.6, 6.5 and 0.6 at 60°C for the (IMA + BA) system. For the (IMA + IA) system the corresponding percentage deviations are 3.2, 7.4 and 2.2 at 30°C ; 0.4, 4.8 and 0.4 at 40°C ; 1.1, 4.7 and 0.5 at 50°C and 1.3, 7.0 and 1.3 at 60°C. For the (BA + IA) system these deviations are 1.0, 1.0 and 1.0 at 30°C ; 1.2, 2.4 and 1.2 at 40°C ; 0, 0 and 0.8 at 50°C, 1.0, 1.0 and 1.0 at 60°C.

Table 11. Experimental* and theoretically calculated values of τ_{mix} by different methods for (IMA + AMA) system at different temperatures.

Temp. (°C)	Mole fraction of IMA in (AMA + IMA)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R.M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E. R.)
30	0.00	6.8	—	—	—	—	—	—
	0.30	6.7	8.3	7.8	8.3	23.9	16.4	23.9
	0.47	9.1	9.1	8.5	9.1	0.0	6.6	0.0
	0.81	11.3	10.8	10.3	10.8	4.4	8.8	4 4
	1.00	11.7	—	—	—	—	—	—
40	0·00	5.6	—	—	—	—	—	—
	0.30	5.4	6.7	6.4	6.7	24.0	18.5	24.0
	0.47	7.3	7.4	6.9	7.3	1.4	5.3	0.0
	0.81	9.3	8.7	8.3	3.5	6.5	10.8	8.60
	1.00	9.4	—	—	—	—	—	—
50	0.00	4.9	—	—	—	—	—	—
	0.30	4.7	5.7	5 4	5.0	21.2	14.9	6.38
	0.47	5.0	6.1	5.8	5.0	22.0	16.0	0.0
	0.81	7.4	7.0	6.8	5.1	5.4	8.1	31.08
	1.00	7.5	—	—	—	—	—	—
60	0.00	4 4	—	—	—	—	—	—
	0.30	4.1	5.0	4.9	4.1	21.9	19.5	0.0
	0.47	3.9	5.4	5.2	3.9	38.5	33.3	0.0
	0.81	6.4	6.1	6.0	3.5	4.7	6.3	45.3
	1.00	6.5	—	—	—	—	—	—

*Data by Gandhi and Sharma (1988).

The data presented in Tables 11, 12 and 13 for the associative + non-associative systems i.e. for (IMA + AMA), (BA + AMA) and (IA + AMA) shows that all the three methods of prediction are equally unsuccessful. For (IMA + AMA) system the average absolute percentage deviations of the calculated τ_{mix} values by S. M., R. M. and eq. (3) methods from the experimental values are respectively 9.4, 10.6 and 9.4 at 30°C ; 10.6, 11.6 and 10.9 at 40°C ; 16.2, 13.0 and 12.5 at 50°C and

21.7, 19.7 and 15.1 at 60°C. These percentage deviations for the (BA+AMA) system are 6.9, 6.9 and 5.9 at 30°C ; 3.9, 3.2 and 2.6 at 40°C ; 1.4, 0.7 and 0.0 at 50°C and 0.0, 0.0 and 0.8 at 60°C. For the (IA+AMA) system, the values for the corresponding deviations are 0.5, 0.5 and 1.0 at 30°C ; 0.6, 0.6 and 0.6 at 40°C ; 2.1, 1.4 and 2.1 at 50°C and 1.7, 1.6 and 1.7 at 60°C. These results show that for a system constituting one associative and another non-associative component the agreement between the experimental and the theoretically

Table 12. Experimental* and theoretically calculated values of τ_{mix} by different methods for (BA+AMA) system at different temperatures.

Temp. (°C)	Mole fraction of BA in (AMA+BA)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 10^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R. M) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R. M.)	% of dev. of τ_{cal_3} (E. R.)
30	0.00	6.8	—	—	—	—	—	—
	0.17	5.7	6.7	6.7	6.7	17.54	17.54	17.54
	0.35	6.6	6.7	6.7	6.6	1.52	1.52	0.0
	0.62	6.5	6.6	6.6	6.5	1.54	1.54	0.0
	1.00	6.4	—	—	—	—	—	—
40	0.00	5.6	—	—	—	—	—	—
	0.17	5.1	5.5	5.5	5.5	7.84	7 84	7.84
	0.35	5.4	5.5	5.5	5.4	1.85	1.85	0.0
	0.62	5.3	5.4	5.3	5.3	1.89	0.0	0.0
	1.00	5.2	—	—	—	—	—	—
50	0.00	4.9	—	—	—	—	—	—
	0.17	4.8	4.8	4.8	4.8	0.0	0.0	0.0
	0.35	4.7	4.8	4.8	4.7	2.12	2.12	0
	0.62	4.6	4.7	4.6	4.6	2.17	0.0	0.0
	1.00	4.5	—	—	—	—	—	—
60	0.00	4.4	—	—	—	—	—	—
	0.17	4.3	4.3	4 3	4.3	0.0	0.0	0.0
	0.35	4.2	4.2	4.2	4.2	0.0	0.0	0.0
	0.62	4.0	4.0	4.0	4.1	0.0	0.0	2.5
	1.00	3.8	—	—	—	—	—	—

*Data by Sharma and Gandhi (1990).

calculated values by all the three methods is of the same order. It appears that in such systems, the change in the molecular environment due to the addition of second component to the first component is very small.

The results presented above show that the empirical method of eq. (3) exhibits a better agreement with the experimental values than the other two computational methods, both in the case of (non-associative+ non-associative) and (associative+

associative) systems. However, for the (associative+non-associative) systems all the three methods are equally competent to predict the experimental results. The apparent drawback with the empirical relation proposed by us is that the knowledge of one τ_{mix} value is essential. The critical assessment of this method will await the availability of sufficient data on several binary systems.

The values of the system characteristic constant A listed in Table 14 show that for (associative+associative) and (non-associative+non-associative) systems, in

Table 13. Experimental* and theoretically calculated values of τ_{mix} by different methods for (IA+AMA) system at different temperatures.

Temp. (°C)	Mole fraction of IA in (AMA+IA)	$\tau_0 \times 10^{12}$ exptal. in secs	$\tau_{cal_1} \times 12^{12}$ (S. M.) in secs	$\tau_{cal_2} \times 10^{12}$ (R. M.) in secs	$\tau_{cal_3} \times 10^{12}$ (E. R.) in secs	% of dev. of τ_{cal_1} (S. M.)	% of dev. of τ_{cal_2} (R.M.)	% of dev. of τ_{cal_3} (E. R.)
30	0.00	6.8	—	—	—	—	—	—
	0.32	6.8	6.8	6.8	6.9	0.0	0.0	1.47
	0.41	6.9	6.8	6.8	6.9	−1.45	−1.45	0.0
	0.64	6.9	6.9	6.9	7.0	0.0	0.0	1.45
	1.00	6.9	—	—	—	—	—	—
40	0.00	5.6	—	—	—	—	—	—
	0.32	5.5	5.6	5.6	5.6	1.82	1.82	1.82
	0.41	5.6	5.6	5.6	5.6	0.0	0.0	0.0
	0.64	5.6	5.6	5.6	5.6	0.0	0.0	0.0
	1.00	5.6	—	—	—	—	—	—
50	0.00	4.9	—	—	—	—	—	—
	0.32	4.9	4.7	4.7	4.7	−4.08	−4.08	−4.08
	0.41	4.6	4.7	4.6	4.6	2.17	0.0	0.0
	0.64	4.5	4.5	4.5	4.4	0.0	0.0	−2.22
	1.00	4.3	—	—	—	—	—	—
60	0.00	4.4	—	—	—	—	—	—
	0.32	4.2	4.2	4.1	4.1	0.0	−2.38	−2.38
	0.41	4.0	4.1	4.1	4.0	2.5	2.5	0.0
	0.64	3.9	4.0	3.9	3.8	2.56	0.0	−2.56
	1.00	3.7	—	—	—	—	—	—

*Data by Sharma and Gandhi (1990).

most of the cases these values are positive and vary between 0.01 and 0.5. For the (associative+non-associative) systems the values of the constant A are mostly negative and around 0.1. The variation in A from system to system does not show any systematic trend. For the same system the constant A shows very little variation with temperature. This suggests that values of A calculated at some lower temperature can be employed to predict τ_{mix} values at higher temperatures.

Thus, on the basis of these results and in absence of sufficient experimental data on mixtures, it is reasonable to conclude that the empirical relation of eq. (3) is dependable for predicting $\bar{\tau}_{mix}$ values. With the availability of more elaborate and accurate experimental data, the validity of eq. (3) may be further ascertained.

Table 14. Values of the constant A of eq. (3) for the various systems.

Systems		A
Benzophenone-tetrahydrofuran	(20°C)	0.01
Chloroform-chlorobenzene	(30°C)	0.46
Bromoform-chlorobenzene	(30°C)	0.24
Bromobenzene-chlorobenzene	(30°C)	0.51
n-Propanol-butanediol-1,3	(−75°C to −27.5°C)	0.11
Glycerol-*n*-propanol	(−75°C to −11.0°C)	−0.48
1,2-Propanediol-dipropylene glycol	(30°C)	0.51
(IMA-BA)	(30°C)	0.47
,,	(40°C)	0.48
,,	(50°C)	0.44
,,	(60°C)	0.44
(IMA-IA)	(30°C)	0.38
,,	(40°C)	0.39
,,	(50°C)	0.40
,,	(60°C)	0.43
(BA-IA)	(30°C)	0.12
,,	(40°C)	0.15
,,	(50°C)	0.06
,,	(60°C)	−0.07
(IMA-AMA)	(30°C)	0.42
,,	(40°C)	0.38
,,	(50°C)	0.03
,,	(60°C)	0.17
(BA-AMA)	(30°C)	−0.09
,,	(40°C)	−0.11
,,	(50°C)	−0.13
,,	(60°C)	−0.15
(IA-AMA)	(30°C)	0.035
,,	(40°C)	0.00
,,	(50°C)	−0.17
,,	(60°C)	−0.26

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